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In re application of: Paul Bruinsma, Suresh Baskaran, Jagannadha R. Bontha, Jun Liu

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For: MESOPOROUS-SILICA FILMS, FIBERS AND POWDERS BY EVAPORATION

Assistant Commissioner for Patents
Washington, D.C. 20231

DECLARATION OF DR. BERG UNDER 37 CFR § 1.132

1. I am a Professor at the University of Washington - Seattle. My responsibilities include teaching at both the graduate and undergraduate level and performing and directing research. I have held this position for 36 years.

2. My education includes a baccalaureate degree in Chemical Engineering from the Carnegie Institute of Technology and a PhD in Chemical Engineering from the University of California - Berkeley. I have received, among other recognitions, the J. S. Guggenheim Memorial Fellowship, the Alpha Chi Sigma Award (a national award for Research in Chemical Engineering) and the University of Washington Outstanding Teacher Award.

3. Previous work experience includes Guest Professor of Technical Chemistry at the Swiss Federal Institute of Technology - Zürich from October, 1974 to October, 1975. My responsibilities included lecturing and research in interfacial phenomena.

4. I am a member of the American Institute of Chemical Engineers, the American Chemical Society (Colloid and Surface Chemistry Division since 1985) and Sigma Xi since 1964. I have performed research on surfactant-containing solutions and have published the following technical articles of interest on surfactant-containing solutions that have relevance to U.S. Patent

No. 5,922,299 to Bruinsma, et al. (hereinafter the Bruinsma patent): (137 papers in interfacial and colloid science, with the following dealing with surfactants or surfactant solutions)

1. Francis, R. C., and Berg, J. C., "The Effect of Surfactants on a Packed Distillation Column," *Chem. Eng. Sci.*, **22**, 685 (1967).
2. Cramer, L. R., and Berg, J. C., "The Effect of Micelles on the Kinetics of the Cannizzaro Reaction," *J. Phys. Chem.*, **72**, 3686 (1968).
3. Sakata, E. K., and Berg, J. C., "Surface Diffusion in Monolayers," *Ind. and Eng. Chem. Fund.*, **8**, 570 (1969).
4. England, D. C., and Berg, J. C., "The Transfer of Surface Active Agents across a Liquid-Liquid Interface," *AIChE J.*, **17**, 313 (1970).
5. Berg, J. C., and Haselberger, G. S., "Mass Transfer during Interfacial Convection," *Chem. Eng. Sci.*, **26**, 481 (1971).
6. Berg, J. C., "Interfacial Phenomena in Fluid Phase Separation Processes," in Recent Developments in Separation Science, II, N.N. Li, Ed., Chem. Rubber Publ. Co., Cleveland, Ohio, pp. 1-31 (1972).
7. Chung, S. T., and Berg, J. C., "Surface Diffusion in Monomolecular Films, I.," *J. Kor. Chem. Eng.*, **10**, 189 (1972).
8. Chung, S. T., and Berg, J. C., "Surface Diffusion in Monomolecular Films, II.," *J. Kor. Chem. Eng.*, **10**, 231 (1972).
9. Palmer, H. J., and Berg, J. C., "Experiments on the Stability of Surfactant Solution Pools Heated from Below," *AIChE J.*, **19**, 1082 (1973).
10. Brumbaugh, K. H., and Berg, J. C., "The Effect of Surface Active Agents on a Sieve Plate Distillation Column," *AIChE J.*, **19**, 1078 (1973).
11. Notter, R. H., and Berg, J. C., "Transport Resistance of Dipalmitoyl Lecithin Monolayers," *J. Colloid Interface Sci.*, **45**, 421 (1973).
12. Dougherty, S. J., and Berg, J. C., "Distribution Equilibria in Micellar Solutions," *J. Colloid Interface Sci.*, **48**, 110 (1974).
13. Dougherty, S. J., and Berg, J. C., "On the Prediction of Reaction Rates in Micellar Solutions," *J. Colloid Interface Sci.*, **49**, 135 (1974).
14. Lim, Y.-C., and Berg, J. C., "Surface Pressure - Area Behavior of Fatty Acid Monolayers on Multicomponent Substrates," *J. Colloid Interface Sci.*, **51**, 162 (1975).
15. MacArthur, B. W., and Berg, J. C., "Surface Equations of State for Insoluble Monolayers on Aqueous Solutions," *J. Colloid Interface Sci.*, **68**, 201 (1979).
16. Smith, R. D., and Berg, J. C., "The Collapse of Surfactant Monolayers at the Air-Water Interface," *J. Colloid Interface Sci.*, **74**, 273 (1980).
17. Baker, G. C., and Berg, J. C., "The Use of Electro-osmotic Dewatering and Soil Chemical Treatment in Frost Heave Reduction," *The Northern Engineer*, **15**, 10 (1984).
18. Ternes, R. L., and Berg, J. C., "The Effect of Monolayer Collapse on Bubble Stability," *J. Colloid Interface Sci.*, **98**, 471 (1984).
19. Berg, J. C., "The Role of Surfactants," in Absorbency, P. Chatterjee, Ed., pp. 149-195, Elsevier, Amsterdam, (1985).
20. Baker, J. A., Parsons, D. A., and Berg, J. C., "Diffusion Effects in the Flocculation of Surfactant-Stabilized Latices by Electrolytes," in Surfactants in Solution, Vol. 6, K.L. Mittal and P. Bothorel, Eds., Plenum Press, New York, pp. 1607-1616 (1986).

21. Hodgson, K. T., and Berg, J. C., "The Effect of Surfactant Adsorption on the Dynamic Wetting of Fibers," in Surfactants in Solution, Vol. 5, K.L. Mittal and P. Bothorel, Eds., Plenum Press, New York, pp. 1113-1120 (1986).
22. Peterson, J. W., and Berg, J. C., "Surface Fractionation of Multicomponent Oil Mixture," *Ind. Eng. Chem. Fundamentals*, **25**, 668 (1986).
23. Maier, H., Baker, J. A., and Berg, J. C., "The Effect of Adsorbed Polymers on the ESA Potential of Aqueous Silica Dispersions," *J. Colloid Interface Sci.*, **119**, 512 (1987).
24. Hodgson, K. T., and Berg, J. C., "The Effect of Surfactants on Wicking Flow in Fiber Networks," *J. Colloid Interface Sci.*, **121**, 22 (1988).
25. Berg, J. C., "The Effect of Surface Active Agents on Distillation Processes," in **Surfactants and Chemical Engineering**, D.T. Wasan, D. Shah, and M.E. Ginn, Eds., pp. 29-76, Marcel Dekker, New York, 1988.
26. Frye, G. C., and Berg, J. C., "Interaction between Surface Active Species in Evanescent Foams," *Chem. Eng. Sci.*, **43**, 1479 (1988).
27. Baker, J. A., and Berg, J. C., "Investigation of the Adsorption Configuration of Poly(ethylene oxide) and its Copolymers with Poly(propylene oxide) on Model Polystyrene Latex Dispersions," *Langmuir*, **4**, 1055 (1988).
28. Frye, G. C., and Berg, J. C., "Antifoam Action by Solid Particles," *J. Colloid Interface Sci.*, **127**, 222 (1989).
29. Baker, J. A., Pearson, R. A., and Berg, J. C., "The Influence of Particle Curvature on Polymer Adsorption Configuration," *Langmuir*, **5**, 339 (1989).
30. Frye, G. C., and Berg, J. C., "Mechanisms for the Synergistic Antifoam Action by Hydrophobic Solid Particles in Insoluble Liquids," *J. Colloid Interface Sci.*, **130**, 54 (1989).
31. Gamon, B. L., Virden, J. W., and Berg, J. C., "The Aggregation Kinetics of an Electrostatically-Stabilized Dipalmitoyl Phophatidylcholine Vesicle System," *J. Colloid Interface Sci.*, **132**, 125 (1989).
32. Chen, W., Fisher, R. R., and Berg, J. C., "Simulation of Particle Size Distribution in an Aggregation-Breakup Process," *Chem. Eng. Sci.*, **45**, 3003 (1990).
33. Einarson, M. B., Aksberg, R., Ödberg, L., and Berg, J. C., "Adsorption and Reconformation of a Series of Cationic Polyacrylamides on Charged Surfaces," *Colloids and Surfaces*, **53**, 183 (1991)
34. Aksberg, A., Einarson, M. B., Berg, J. C., and Ödberg, L., "Adlayer Thickness of Two Cationic Polyacrylamides Adsorbed onto Polystyrene Latices," *Langmuir*, **7**, 43-45 (1991).
35. Miller, N. P., and Berg, J. C., "A Comparison of Electroacoustic and Microelectrophoretic Zeta Potential Data for Titania in the Absence and Presence of a Poly (Vinyl Alcohol) Adlayer," *Colloids and Surfaces*, **59**, 119 (1991).
36. Chen, W., Walker, S., and Berg, J. C., "The Mechanism of Floc Formation in Protein Precipitation by Polyelectrolytes," *Chem. Eng. Sci.* **47**, 1039 (1992).
37. Virden, J. W., and Berg, J. C., "The Use of Photon Correlation Spectroscopy for Estimating the Rate Constant for Doublet Formation in an Aggregating Colloidal Dispersion," *J. Colloid Interface Sci.*, **149**, 528 (1992).
38. Virden, J. W., and Berg, J. C., "The NaCl-Induced Aggregation of Dipalmitoyl Phosphatidylglycerol Small Unilamellar Vesicles with Varying Amounts of Incorporated Cholesterol," *Langmuir*, **8**, 1532 (1992).
39. Williams, D. F., and Berg, J. C., "The Aggregation of Colloidal Particles at the Air-Water Interface," *J. Colloid Interface Sci.*, **152**, 218 (1992).

40. Virden, J. W., and Berg, J. C., "The Steric Stabilization of Small Unilamellar Vesicles," *J. Colloid Interface Sci.*, 153, 411 (1992).
41. Einarson, M. B., and Berg, J. C., "The Effect of Salt on Polymer Solvency: Implications for Dispersion Stability," *Langmuir*, 8, 2611 (1992).
42. Einarson, M. B., and Berg, J. C., "Electrosteric Stabilization of Colloidal Latex Dispersions," *J. Colloid Interface Sci.*, 155, 165 (1993).
43. Chen, W., and Berg, J. C., "The Effect of Polyelectrolyte Dosage on Floc Formation in Protein Precipitation by Polyelectrolytes," *Chem. Eng. Sci.*, 48, 1775 (1993).
44. Snyder, B. A., Schmidt, D. C., and Berg, J. C., "Characterization and Flotation Studies of Electrostatic Inks," *Progress in Paper Recycling.*, 3 [1], 17 (1993).
45. Seebergh, J. E., and Berg, J. C., "Depletion Flocculation of Aqueous, Electrosterically Stabilized Dispersions," *Langmuir*, 10, 454 (1994).
46. Epple, M., and Berg, J. C., "The Effect of Adsorbed Surfactants on the Electrostatic Properties and Wettability of a Xerographic Toner," *Prog. in Paper Recycling.* 3 [2], 52 (1994).
47. Seebergh, J. E., and Berg, J. C., "Evidence of a Hairy Layer at the Surface of Polystyrene Latex Particles," *Colloids and Surfaces*, 100, 139 (1995).
48. Sunkel, J. M., and Berg, J. C., "The Stability Behavior of Sol-Emulsion Systems," *Journal of Colloid and Interface Science*, 179, 618 (1996).
49. Seebergh, J. E., and Berg, J. C., "The Effect of Organic Cosolvent on the Aggregation Stability of an Aqueous Polystyrene Latex Dispersion," *Colloids and Surfaces* , 121, 89 (1997).
50. Stenkamp, V. S., and Berg, J. C., "The Role of Long Tails in Steric Stabilization and Hydrodynamic Layer Thickness," *Langmuir* , 13, 3827 (1997).
51. Kim, A. Y., and Berg, J. C., "Fractal Heteroaggregation of Oppositely Charged Colloids," *J. Colloid Interface Sci.*, 229, 607 (2000).
52. Stenkamp, V.S., McGuiggan, P.M., and Berg, J.C., "Restabilization of Electrosterically Stabilized Colloids in High Salt Media," *Langmuir* (accepted Oct., 2000).
53. Daniel, R., and Berg, J. C., "Diffusion-Controlled Adsorption at the Liquid-Air Interface: the Long-Time Limit," *J. Colloid Interface Sci.* (submitted Sept. 22, 2000).

5. I have thoroughly studied and understand the Bruinsma patent, the filing date of which was August 26, 1997, and am aware of the patents and technical publications cited in the Background section thereof. I also have a working knowledge of the general field of interfacial and colloid science, including surfactant solutions and self-assembled structures formed therein.

6. I have thoroughly studied and understand U.S. Patent No. 5,858,457 to Brinker, et al. (hereinafter the Brinker patent), the filing date of which was September 25, 1997, and am aware of the patents and technical publications cited in the Background section thereof.

7. I am an expert in the field of interfacial and colloid science, including surfactant solutions and self-assembled structures formed therein.

8. Silica or SiO2 been referred to or classified under metal oxides in the technical literature for over ten years. One of ordinary skill in the art would have known in August 26, 1997 that metal oxide was the general class of oxides referred to in the Bruinsma patent. This is evident from the textbook published by Brinker (C. J. Brinker and G. W Scherer, Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing, p. 97 (1990), attached hereto as Ex. A) where it is mentioned that "silicon is the most abundant metal in the earth's crust," and thus silicon dioxide or silica SiO2 falls generally within the broad category of metal oxides. Indeed, the Brinker patent filed September 25 1997 assumes that silica oxides are within the broad metal oxide category: Brinker says at column 6, lines 7 through 9 in the patent that "[a]lthough silica sols are discussed primarily here, *other metal oxides* can be used in the preparation of these thin films… ." This September 27, 1997 understanding by one of ordinary skill in the art is further evidence that on August 26, 1997—just slightly more than one month earlier--it was well known that silicon dioxide is just one example of a range of metal oxides.

9. Cationic surfactants are referred to as "preferred" surfactants in the Bruinsma patent at column 7, lines 40-52. One of ordinary skill in the art on August 26, 1997 would have known that other surfactants, e.g. anionic or non-ionic or amphoteric, can be usefully employed in substitution therefor in the described process for forming mesoporous films. This is because other surfactants, including non-ionic surfactants, had already been used to make mesoporous powders (See, for example, S. A. Bagshaw, E. Prouzet, T. J. Pinnavia, Science, Vol. 269, p. 1242 (1995), attached hereto as Exhibit B). Further, the surfactants described in the Bruinsma patent would be understood to be 'free' surfactants in the sense of the Brinker patent's use of the term. Brinker means free as opposed to micellar surfactants. This same freedom characterizes the surfactants used in the Bruinsma patent to form a mesoporous film (See expert Declaration of Jun Liu regarding surfactant concentration below CMC, attached hereto as Exhibit C.).

10. Catalysts are typically either base or acid, and those of skill in the art of sol gel synthesis would have been well aware of the possible substitution of a base catalyst, as described in the

alternative in the Brinker patent, for the described acid catalyst of the Bruinsma patent on August 26, 1997. This is because the use of base catalysts had been already reported for synthesizing mesoporous powders using surfactants and inorganic precursors. (See, for example, Kresge, C. T., Leonowicz, M. E., Roth, W. J., Vartuli, J. C., & Beck, J. S. *Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism*, Nature, Vol. 359, pp. 710–712 (1992), attached hereto as Exhibit D).

11. Aqueous solvents as described in the Bruinsma patent would have been understood by those of ordinary skill to be water mixed with one or more other solvents, e.g. alcohol. The use of such an aqueous solvent is convenient for synthesis of film from a sol precursor. Organic solvents, as described in the Brinker patent, are simply an organic solvent containing one or more other solvents including water. Brinker's examples all used water-alcohol mixtures, and thus Brinker's organic solvents are nothing other than aqueous solvents described in the Bruinsma patent's examples and claims.

12. It would be reasonable for one of ordinary skill in the art to assume that the silica precursors described in the Bruinsma patent could be substituted by similar metal oxides. This had been demonstrated already much earlier than 1996 in general synthesis of mesoporous materials. (See, for example, Q. Huo, D. I. Margolese, U. Ciesla, P. Peng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schuth, G. D. Stucky, Generalized synthesis of periodic surfactant/inorganic composite materials, Nature, Vol. 368, p. 317 (1994), attached hereto as Exhibit E).

13. The solutions used to deposit films in the examples of Bruinsma use a water-to-TEOS, i.e. water-to-silicon, molar ratio of 7-to-1. (TEOS is the tetraorthosilicate precursor containing one Si atom in one molecule of the TEOS.) This is higher than the water-to-Si molar ratio of 2 that is theoretically sufficient, i.e. the stoichiometric ratio, for complete reaction to form anhydrous silica. (See, for example, C.J. Brinker and G.W. Scherer, Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing, pp. 108-110 at 109 (1990), attached hereto as Exhibit F.) So the excess water used in Bruinsma simply indicates a superstoichiometric amount of water with respect to the TEOS.

14. Surfactant-templated materials have been calcined over a wide range of temperature from 400°C to over 650°C. (See, for example, U.S. Patent No. 5,622,684 to T.J. Pinnavaia and S.A. Bagshaw, entitled *Porous Inorganic Oxide Materials Prepared by Non-ionic Surfactant Templating Route*, and issued April 22, 1997, attached hereto as Exhibit G.) In the semiconductor manufacture process, wafer processing temperatures during application of dielectric films generally should not exceed approximately 400-450°C for significant periods of time. This is because the transistor and other devices within the silicon substrates can be damaged by excessive heating. Furthermore high temperature treatments much higher than about 450°C can damage the integrity and performance of overall device structure containing porous films and other features in a microelectronic device. The Bruinsma patent describes the use of 450°C calcination temperature in one example. Anyone with ordinary skill in the art in August 1997 would logically conclude that the material could just as easily have been calcined at any temperature from 400°C to 450°C.

15. I, the undersigned, declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated this 6TH day of NOVEMBER, 2000.

John C. Berg

J.C. Berg
Professor
Of University of Washington, Seattle